Available online at www.sciencedirect.com

SciVerse ScienceDirect

Energy Procedia 23 (2012) 64 – 71

Energy Procedia

TCCS-6

# Solvents with low critical solution temperature for $CO_2$ capture

Zhicheng Xu, Shujuan Wang[a]*, Jinzhao Liu and Changhe Chen

*Key laboratory for thermal science and power engineering of Ministry of Education*
*Department of Thermal Engineering, Tsinghua University, Beijing 100084, China*

**Abstract**

The absorption and desorption characteristics of five amine solutions with low critical solution temperature were tested, analyzed and compared with 5M MEA using a fast screening experiment system. The results showed that among these solvents, 5M N-Ethylmethallylamine (EMAA) has the fastest initial absorption rate, 3M Triethylamine (TEA) has the largest carrying capacity, and 2M Diisopropylamine (DIPA) has the highest $CO_2$ removal efficiency with relatively high absorption rate. 2M DIPA shows the best performance based on the combined analysis. None of these five amines show phase transition during absorption at 40 $^oC$, while 3M TEA and 5M Diallylamine (DAA) become two phases after desorption, and can keep being two phase after cooling to room temperature.



Keywords: $CO_2$ absorption, desorption, solvent, low critical solution temperature

## 1. Introduction

As global climate change is becoming a more important issue, the technology which can reduce $CO_2$ emission is attracting more and more attentions. Several different kinds of technologies exist for $CO_2$ capture. Among them, amine based absorption is the most attractive one today for its high flexibility and easy retrofit for existing power plant [1]. The solvent development is regarded as one of the most crucial issues for post combustion $CO_2$ capture. Many solvents, such as monoethanolamine (MEA), methyldiethanolamine (MDEA), diethanolamine (DEA) and piperazine (PZ), have been applied to capture

* Corresponding author. Tel.: +86-10-62788668; fax: +86-01-62770209.
*E-mail address*: wangshuj@tsinghua.edu.cn

 doi:10.1016/j.egypro.2012.06.045

$CO_2$[2][3][4]. However, this process always requires lots of energy during the desorption. Therefore, the key problems are, how to reduce the energy penalty, and then how to reduce the cost. Recently, some novel concepts, such as DMX$^{TM}$[5] and lipophilic amine solvents[6], have been proposed for the improvement of the energy performance. Zhang et al[7] tested DMA, DMCA and other solvents for screening. Tan[8] studied kinetics and thermodynamic of the blend of DPA and DMCA, and found the cyclic loading of the solvent could reach 0.7 mol $CO_2$/mol amine. Raynal el al[5] proposed the concept of DMX$^{TM}$ process, which, according to their previous simulation, could remarkably reduce the reboiler duty to 2.3GJ/t$CO_2$. Bruder el al[9] found that the blend of 5M DEEA and 2M MAPA could get two phases after $CO_2$ absorption and the cyclic loading was higher than that of 5M MEA. All of these systems have many requirements on the characteristics of the solvent, amongst of which, as the previous researchers pointed out, low critical solution temperature (LCST) is the most important one. LCST is a critical temperature below which the mixture is miscible in all proportions. It may be resulted from associating interactions and compressibility effects.

This work aims to investigate the absorption and desorption properties of five amine solutions with LCST and compare with traditional 5M MEA using a fast screening facility. The five amines are 2M Diisopropylamine (DIPA), 2M and 5M N-Ethyl-n-butylamine (EBA), 3M Triethylamine (TEA), 5M Diallylamine (DAA), and 5M N-Ethylmethallylamine (EMAA). The LCST and boiling points (BP) of these five amine solutions have been reported [10] and are listed in Table 1. The reason to lower the concentration of some amine solutions to 2M or 3M is due to the high volatility.

Table 1. LCST and boiling point of selected amine solvents

| solvent | DIPA | EBA | TEA | DAA | EMAA |
|---|---|---|---|---|---|
| LCST/ $^{o}$C | 28 | 15 | 18 | 6 | 18.6 |
| BP/ $^{o}$C | 84 | / | 88.8 | 111 | 105 |

## 2. Experimental

### *2.1. Materials*

The amines used in this experiment are MEA (≥99wt%) , EBA (≥99wt%), TEA (≥99.5wt%), DAA (≥99wt%), EMAA (≥98wt%), DIPA (≥99.5wt%). All of them were from Sigma–Aldrich and prepared with deionised water without further purification. $N_2$ (≥99.99%, vol) and $CO_2$ (≥99%, vol) were from Beijing Huayun Gas Company.

### *2.2. Experiment system*

The experiments were carried out in a fast screening facility to quickly evaluate the performance of the solvents and compare them with MEA. As Fig.1 shows, this apparatus can be used for both absorption and desorption. On “absorption mode”, $CO_2$ and $N_2$, controlled by mass flow controller were used to simulate the flue gas, with 12% of $CO_2$ in terms of volume. The total gas rate was 463 ml/min. The simulated flue gas went through the gas mixing tank first to mix intensively, and then to the reactor, which was made of glass and had a volume of about 150ml. The outlet gas went through the condenser, acid washing, drier, and IR analyser before venting. The condenser was cooled by 3 $^{o}$C water. The condensate went back to the reactor to avoid water losses. The red line in Fig.1 means the pipeline was heated during the experiment. The absorption temperature was controlled at 40 $^{o}$C by water bath, and the

pressure was 1 atm. On "desorption mode", $N_2$ was used to sweep the desorbed $CO_2$. The temperature and pressure was 80 °C and 1atm, respectively.

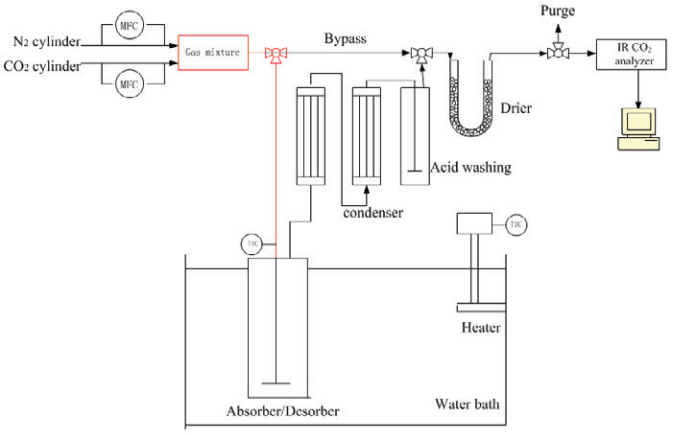


Fig.1 Experiment system

### *2.3. Calculation method*

For absorption, since the flow rates of $CO_2$ and $N_2$ from gas cylinders are well controlled and measured by the mass flow controller, $CO_2$ flow rate after absorption can be calculated by Equation 1.

$$Q_{CO_2} = \frac{Q_{N_2}}{1 - C_{CO_2}} - Q_{N_2} \tag{1}$$

Where, $Q_{CO_2}$ and $Q_{N_2}$ are flow rate of $CO_2$ and $N_2$ after absorption, mol/s. $C_{CO_2}$ is mol fraction of $CO_2$ in the feed gas.

Absorption rate and absorption capacity were calculated with Equation 2 and 3,

$$r_{abs} = \frac{Q_{CO_2}^{out} - Q_{CO_2}^{in}}{V} \tag{2}$$

$$R_{\text{abs}} = \int_0^t r_{abs} \tag{3}$$

Where, $r_{abs}$ is $CO_2$ absorption rate, $mol \bullet L^{-1} \bullet s^{-1}$; $R_{abs}$ is absorption capacity of the solution, mol/L; $Q_{CO_2}^{out}$ and $Q_{CO_2}^{in}$ are $CO_2$ flow rate at inlet and outlet of the absorber, mol/s; $V$ is the volume of solution, L; $t$ is the absorption time, second(s).

Loading of rich solution, $\alpha_{rich}$ is determined by Equation 4, in which $c_{a\,\text{min}\,e}$ means amine concentration, mol/L.

$$\alpha_{rich} = R_{abs} / c_{a\,\text{min}\,e} \tag{4}$$

For desorption and combined analysis, desorption capacity and $CO_2$ concentration in the solution after desorption are considered, and calculated by Equation 5 and 6, respectively.

$$R_{\text{des}} = n_{CO_2}^{des} / V \tag{5}$$

$$c_{CO_2}^{des} = \alpha_{lean} \times c_{amine} \tag{6}$$

Where, $R_{des}$ is desorption capacity, mol/L; $n_{CO_2}^{des}$ is $CO_2$ desorbed from the solution, mol; $c_{CO_2}^{des}$ is $CO_2$ concentration in the solution after desorption, mol/L;

$CO_2$ removal capacity and $CO_2$ removed per cycle can be calculated with Equation 7 and 8,

$$\Delta R = R_{abs} - c_{CO_2}^{des} \tag{7}$$

$$\eta = \Delta\alpha / \alpha_{rich} \tag{8}$$

Where, $\Delta R$ is $CO_2$ removal capacity, mol/L; $\Delta\alpha$ is cyclic loading, that is, the difference of rich and lean loading. $\eta$ is the result of cyclic loading divided by rich loading.

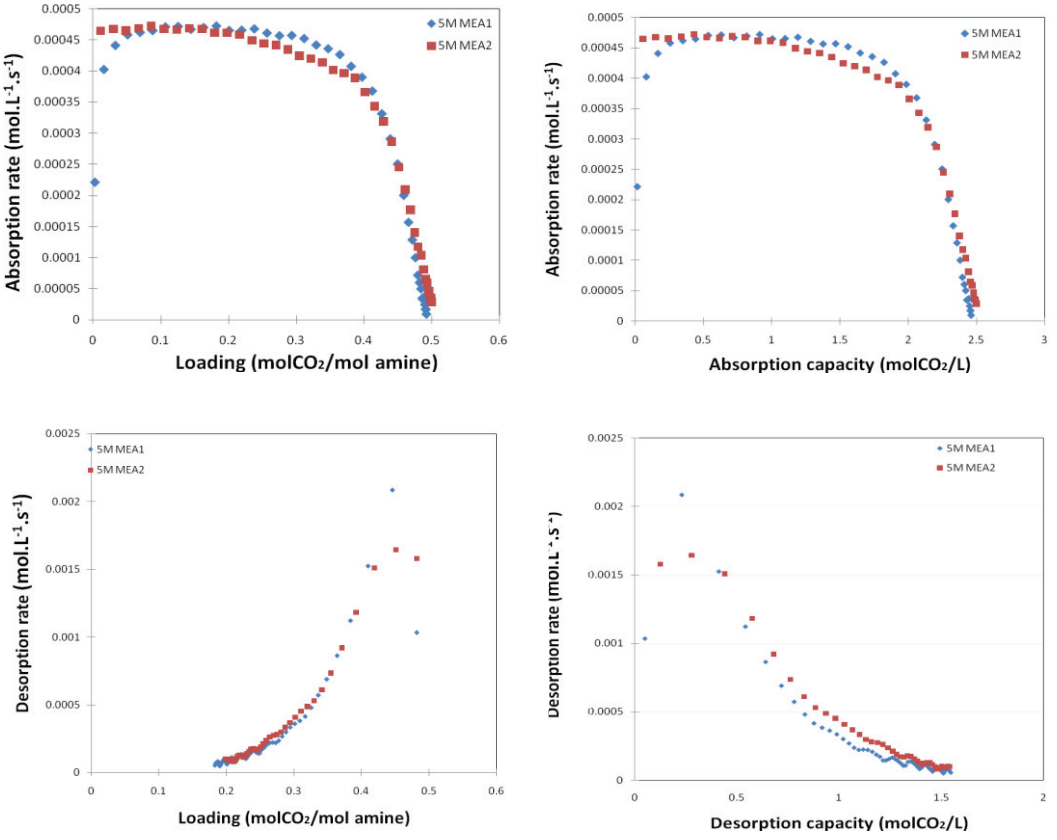


Fig.2 Repeated trail of 5M MEA

*2.4. Repeated trial using 5M MEA*

Before screening test, 5M MEA was used for repeated trial. The results can be seen in Fig. 2. The blue line and red line represent two separate experiments under totally same conditions. From this Figure, we

can see that the two lines are very close, which means the system has good repeatability. After each test, the loading of rich and lean solution was titrated using barium carbonate precipitation method and compared with calculation results got by the above equations. The calculation results of rich and lean loading were 0.492 and 0.182 respectively, while the titration results were 0.483 and 0.182, thus we can conclude that this screening system has very good accuracy and repeatability.

## 3. Results and discussion

### *3.1. Absorption*

The relationship between absorption rate and $CO_2$ loading of these solvents is shown in Fig.3 (a). The Figure shows that the performance of 2M DIPA and 2M EBA is better than 2.5M and 5M MEA in terms of both absorption rate and rich loading, while 3M TEA and 5M DAA are worse. The absorption rate of 5M EMAA is higher than that of MEA, but rich loading is reverse. 2M DIPA can reach the highest absorption rate and rich loading of 0.736, because it is secondary amine and has more side chains.

Absorption capacity is another important parameter to evaluate the solvent performance. Absorption rate versus absorption capacity is presented in Fig.3(b), which shows that all the 5M solution, except 5M DAA, performed very well in terms of absorption capacity. It is obvious that 5M solution have more amine than 2M and 3M solutions per liter, so they can obtain higher absorption capacity. For the exception of 5M DAA, possible reason is its two double bonds and more degradation. We can also observe that the absorption capacities of 2M EBA and 2M DIPA are higher than that of 2.5M MEA, which can be explained by the longer carbon chain.

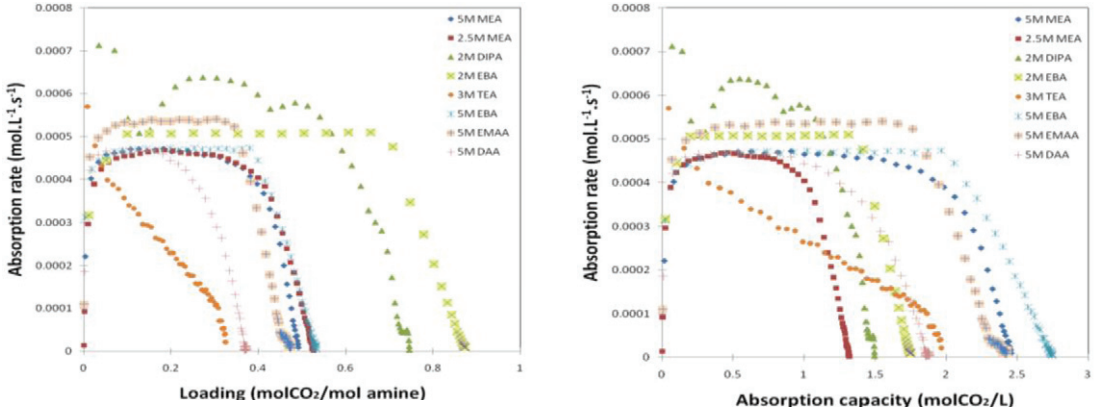


Fig. 3 (a) Relationship between absorption rate and loading; (b) Relationship between absorption rate and absorption capacity.

### *3.2. Desorption*

As to desorption rate and lean loading, Fig.4(a) shows that 5M DAA performed the best, followed by 3M TEA, 2.5M MEA, and 2M DIPA, with the lean loading of 0.087, 0.116, 0.124, and 0.125 mol$CO_2$/mol amine, respectively. However, considering the rich loading, absorption rate and absorption capacity, 5M DAA is not very promising for biphasic solvent.

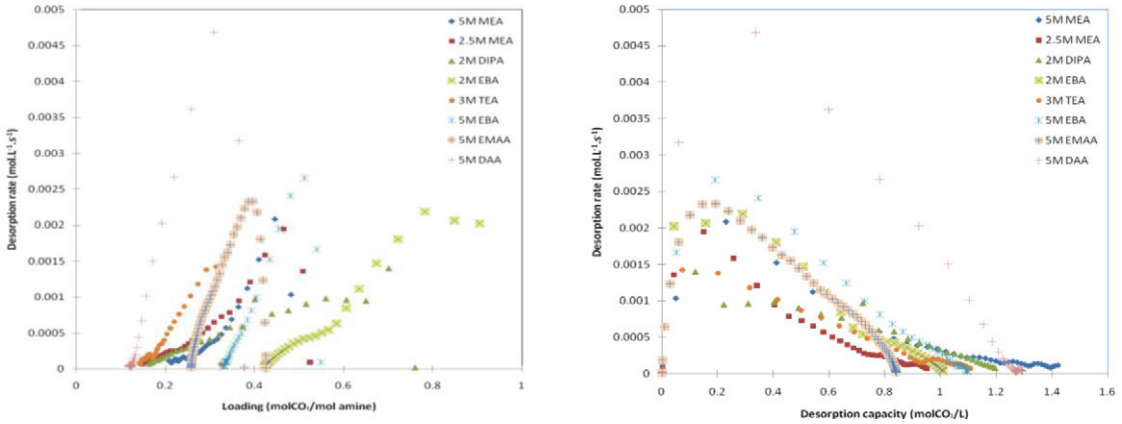


Fig. 4 (a) Desorption rate as a function of loading; (b) Desorption rate as a function of desorption capacity

Fig.4 (b) shows curves of desorption rate versus desorption capacity. We can observe that 5M MEA is the best one among them, with the highest desorption capacity of 1.42 mol$CO_2$/L solution and the comparatively rapid desorption rate.

### *3.3. Combined analysis*

As it is difficult to select which one is the most promising by considering only one characteristics of the solvent, the combined analysis conveyed by dot plots was used to evaluate the overall performance of selected solvents[11][12], as Fig.5 shows. The right corner at the top of the Figure should be the best one.

Fig.5 (a) gives a comparison of all the solvents with respect to absorption rates at lean loading and $CO_2$ removal percentage per cycle. It shows that 5M EMAA have the highest absorption rate at lean loading, followed by 2M EBA and 2M DIPA. As for the $CO_2$ removed per cycle, however, 2M DIPA is much better than 5M EMAA and 2M EBA. Absorption rate at lean loading was plotted against $CO_2$ removal capacity in Fig.5 (b). It shows that for certain volume of the solution, 3M TEA can remove more $CO_2$ per cycle. Its reaction rate, however, is not as fast as that of 2M DIPA. In order to evaluate the reaction rate of the solvents, both at lean and rich loading, absorption rate at lean loading was plotted as a function of absorption rate at 90% equilibrium loading. As Fig.5(c) shows, 2M DIPA has the highest absorption rate when approaching equilibrium, and has slightly lower absorption rate at lean loading than 5M EMAA. We can also know that 2M DIPA performs better than 2.5M and 5M MEA in terms of absorption rate at both lean and 90% equilibrium loading. Regarding to $CO_2$ removal capacity and removal percentage per cycle, as Fig.5(d) shows, 3M TEA, 5M DAA and 2M DIPA have better performances when we consider these two aspects together.

Above all, 2M DIPA appears to perform the best based on the combined analysis. It shows high reaction rate at lean and rich loading, highest removal efficiency per cycle (around 83%). Its cyclic loading is 0.611mol $CO_2$/mol solution, and 1 liter solution can remove 1.22 mol $CO_2$ per cycle.

### *3.4. Observed characteristics*

None of these five amines showed phase transition during absorption at 40 $^oC$. 3M TEA and 5M DAA became two phases after desorption, and maintained this status when cooling to room temperature, which

indicates that they are potential solvents for the auto-extraction system mentioned in literature[8]. For all the solvents tested, except for 3M TEA, there was almost no solvent loss.

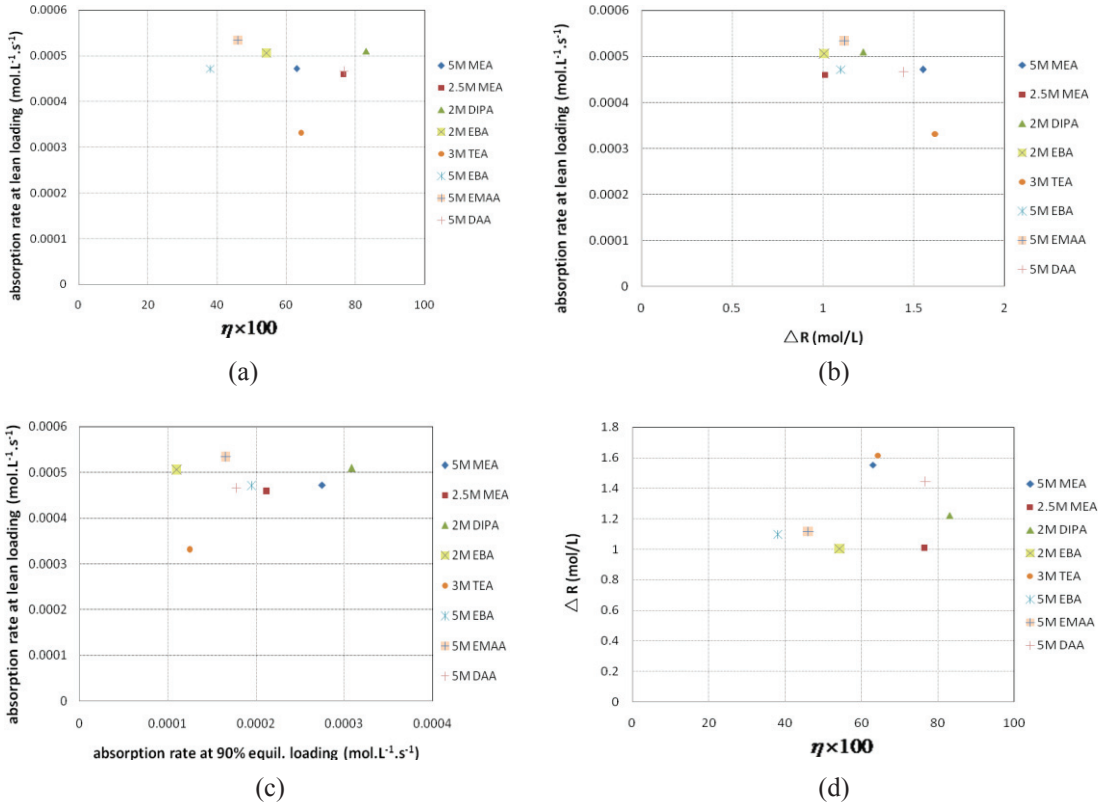


Fig.5 (a) Absorption rate at lean loading versus $CO_2$ removed per cycle; (b) Absorption rate at lean loading versus $CO_2$ removal capacity; (c) Absorption rate at lean loading versus absorption rate at 90% equilibrium loading; (d) $CO_2$ removal capacity versus $CO_2$ removed per cycle

## 4. Conclusions

A fast solvent screening experiment system was established, and some screening standards were given. The system showed good repeatability and agreed well with barium chloride precipitation titration. Five amine solutions with low critical solution temperature were tested, analyzed and compared with 5M MEA using the fast screening experiment system. Among them, 2M DIPA showed the best performance based on the combined analysis. All these five amines' phase transition disappeared with the increase of $CO_2$ concentration. 3M TEA and 5M DAA became two phases after desorption, which indicates that they may be promising for auto-extraction system.

## Acknowledgements

Financial support from the National Natural Science Foundation Project of China (50876051) is gratefully acknowledged.

## References

[1] Gary T. Rochelle. Amine scrubbing for $CO_2$ capture. *Science* 2009;**325**:1652-1654

[2] Edward B. Rinker, Sami S. Ashour et al. Absorption of carbon dioxide into aqueous blends of diethanolamine and methyldiethanolamine. *Ind. Eng. Chem. Res.* 2000;**39**:4346-4356.

[3] P.W.J. Derks, H.B.S. Dijkstra et al. Solubility of carbon dioxide in aqueous piperazine solutions. *Thermodynamics* 2005;**51**:2311–2327.

[4] Sanjay Bishnoi, Gary T. Rochelle. Absorption of carbon dioxide in aqueous piperazine/methyldiethanolamine. *American Institute of Chemical Engieers.AIChE Journal* 2002;**48**:2788–2799.

[5] Ludovic Raynal, Pascal Alix et al. The DMX$^{TM}$ process: An original solution for lowering the cost of post-combustion carbon capture. *Energy Procedia* 2011;**4**:779–786.

[6] Xiaohui Zhang. Studies on multiphase $CO_2$ capture system. *Ph.D dissertation.University of Dortmund,* 2007.

[7] Jiafei Zhang, David W. Agar et al.$CO_2$ absorption in biphasic solvents with enhanced low temperature solvent regeneration. *Energy Procedia* 2011;**4**:67–74.

[8] Yudy Halim Tan. Study of $CO_2$-absorption into thermomorphic lipophilic amine solvents. *Ph.D dissertation.University of Dortmund,* 2010

[9] Peter Bruder, Hallvard F. Svendsen. Solvent comparison for postcombustion $CO_2$ capture. 1$^{st}$ Post Combustion Capture Conference. Abu Dhabi, Kingdom of Saudi Arabia. May 17-19, 2011.

[10] Richard M. Stephenson. Mutual Solubilities: water+cyclic amines, water+alkanolamines and water+polyamines. *J Chem. Eng. Data.* 1993;**38**:634–637.

[11] Sholeh Ma'mun, Hallvard F. Svendsen et al. Selection of new absorbents for carbon dioxide capture. *Energy Conversion and Management* 2007;**48**:251–258.

[12] Ugochukwu E. Aronu, Hallvard F. Svendsen et al. CO2 capture solvent selection by combined absorption-desorption analysis. *Chemical Engineering Research and Design* 2011;**89**:1197–1203.